

Methacrylic Esters of Glucose and Other Carbohydrates¹

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Recently methacrylic anhydride became available for research purposes. Although methacrylic esters of lower aliphatic alcohols have been of technical importance for some time, none has been prepared with methacrylic anhydride. Properties of methacrylic esters of the starch group of carbohydrates (glucose, maltose, dextrin, and starch) prepared by us are described here.

Preparation and Properties of Glucose Pentamethacrylate.—Thirty grams of glucose was stirred into 150 g. of pyridine at 65°. Methacrylic anhydride (192 g.) was added gradually. This amount is 50% more than that required for penta substitution. The sugar dissolved entirely in about three hours, but stirring and heating were continued for another half hour. The solution was then poured into stirred cold water. The sirup which separated was washed with water several times and then dissolved in warm alcohol. On cooling, twenty grams of fine needle-shaped white crystals of glucose pentamethacrylate separated. The substance was soluble in alcohol, acetone, benzene, chloroform, and other organic solvents, but insoluble in aliphatic hydrocarbons. After two recrystallizations, a constant melting point was attained, 115° (cor.). The specific rotation for a 4% solution in absolute alcohol was $[\alpha]_D^{25} +87.3^\circ$.

Anal. Calcd. for $C_{26}H_{32}O_{11}$: C, 60.0; H, 6.2. Found: C, 59.8; H, 6.1. Calcd. for $C_6H_7O_6(CH_2=C(CH_3)CO-)_5$: methacrylyl, 66.4. Found by saponification: methacrylyl, 66.4.

Solutions of glucose pentamethacrylate in chloro-

form and other solvents gel in the presence of benzoyl peroxide or cobalt naphthenate. The fact that both these agents accelerate polymerization of glucose pentamethacrylate suggests that besides the addition polymerization, polymerization accompanied by oxidation takes place. This was further substantiated by the following experiments. After a month at room temperature, glucose pentamethacrylate crystals were still soluble in organic solvents, but combustion analysis showed only 57.8% carbon, which corresponds approximately to the original compound with one atom of oxygen added. After being heated for two hours at 100°, glucose pentamethacrylate became insoluble in all organic solvents. The carbon value was 54.2%, indicating the addition of approximately 3 atoms of oxygen.

Maltose octamethacrylate was prepared as an amorphous powder by the procedure used for glucose. It was soluble in the same solvents as glucose pentamethacrylate. Analysis showed 62.5% methacrylyl (calcd., 62.3%); specific rotation $[\alpha]_D^{25} +81.4^\circ$ in 4% solution in alcohol. A solution of maltose octamethacrylate (50% in chloroform) gelled in fifteen days at room temperature, in four in the presence of benzoyl peroxide, and in two in the presence of cobalt naphthenate. The amorphous powder became insoluble in one to two weeks at room temperature and in about two hours when heated at 100°.

Dextrin trimethacrylate was prepared in a similar manner (six hours at 95°). The amorphous powder was insoluble in alcohol and aliphatic hydrocarbons but soluble in most other usual solvents. It insolubilized on exposure to air.

Starch methacrylate (substitution 2.9) was prepared (seven hours at 95°) as an amorphous powder insoluble in most solvents but slightly soluble in pyridine and tetrachlorethane. It became entirely insoluble on exposure to air or after short heating.

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